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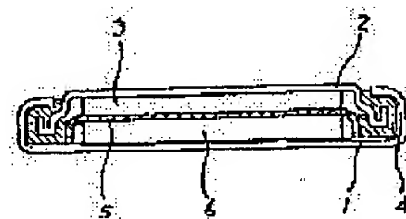
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(54) ORGANIC ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PURPOSE: To improve electrochemical stability of an electrolytic liquid by providing a positive pole and a negative pole prepared from a material which absorbs and desorbs lithium ion and using a mixed liquid of sulfolane and ethylene carbonate as a solvent of an electrolytic liquid.

CONSTITUTION: A positive pole 6 consisting of mainly a lithium-cobalt composite oxide which absorbs and desorbs lithium ion is set in the inside of a case 1 which works also as a positive pole terminal and is made of a stainless- aluminum-clad steel sheet and a negative pole 3 which is made of a carbon material and absorbs and desorbs lithium ion is brought into contact with a separator while setting a separator 5 of polypropylene impregnated with an organic electrolytic liquid between the poles and the case 1 is sealed by a sealing sheet 2 which is made of the same kind of a material as that of the case 1 and works also as a negative pole terminal while the gap between the case and the sheet 2 is filled with a gasket 4. As the organic electrolytic liquid, a solution prepared by dissolving lithium perchloride in a mixed solvent of sulfolane and ethylene carbonate is used and it is poured in the positive and the negative pole sheets and the separator.



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CLAIMS

[Claim(s)]

[Claim 1] The positive electrode which consists of matter which carries out occlusion discharge of the lithium ion, and the carbon material which carries out occlusion discharge of the lithium ion are set to the organic electrolytic-solution rechargeable battery which it had as a negative electrode, and it is a sulfolane (S). Organic electrolytic-solution rechargeable battery characterized by using a mixed solvent with ethylene carbonate (EC) as an electrolytic-solution solvent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the organic electrolytic-solution rechargeable battery which is the high energy density as the power supply for a drive, the memory maintenance power supply, or the power supply for electric vehicles of electronic equipment, and has high safety.

[0002]

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. Furthermore, an electric vehicle is attracting attention with a rise of the interest about an environmental problem in recent years, also to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which the repeat charge and discharge under an elevated temperature (temperature of 85 degrees C) are still more possible is increasing. As a rechargeable battery which fills these demands, an organic electrolytic-solution rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of an organic electrolytic-solution rechargeable battery. Especially, they are a lithium cobalt multiple oxide (Li_xCoO_2) and a spinel type lithium manganic acid ghost ($\text{Li}_x\text{Mn}_2\text{O}_4$). 4V (Li/Li+) Since [above] charge and discharge are extremely performed by electropositive potential, the cell which has high discharge voltage is realizable by using as a positive electrode.

[0004] As for the negative-electrode active material of an organic electrolytic-solution rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] however, a positive electrode -- a lithium cobalt multiple oxide (LiCoO_2) and spinel type lithium manganic acid ghost ($\text{Li}_x\text{Mn}_2\text{O}_4$) etc. -- the cell which used and used the carbon material for the negative electrode had the problem that service capacity fell rapidly with advance of the charge-and-discharge cycle under an elevated temperature (temperature of 85 degrees C) For example, propylene carbonate (PC), and 1 and 2-dimethoxyethane (DME) It is a lithium perchlorate (LiClO_4) to a mixed solvent. When the coin cell using the electrolytic solution which dissolved repeated charge and discharge, service capacity decreased rapidly. This is considered to originate in oxidative degradation of the electrolytic solution having been carried out by the positive electrode.

[0006] They are propylene carbonate (PC) and diethyl carbonate (DEC) as the organic electrolytic solution which was excellent in usable oxidation-resistant ability in the fuel cell subsystem of such a high voltage recently. When the mixed solvent was used, it was reported that the fall of the aforementioned service capacity is suppressed (collection [of the 32nd cell debate summaries] p.31 (1991)).

[0007] However, as a result of our examining the above-mentioned electrolytic solution, it turns out that there is still electrochemical stability of the above-mentioned organic solvent insufficiently.

[0008] Then, the development of the electrolytic solution which improved the electrochemical stability of the electrolytic solution further was called for.

[0009]

[Means for Solving the Problem] this invention sets the positive electrode which consists of matter which carries out occlusion discharge of the lithium ion, and the carbon material which carries out occlusion discharge of the lithium ion to the organic electrolytic-solution rechargeable battery which it had as a negative electrode, and is a sulfolane (S). By using a mixed solvent with ethylene carbonate (EC), it is going to solve the above-mentioned trouble.

[0010]

[Function] The organic electrolytic-solution rechargeable battery of this invention has operation that the maintenance property of the service capacity at the time of repeating a charge-and-discharge cycle under an elevated temperature as compared with the conventional organic electrolytic-solution rechargeable battery is excellent. This is considered to originate in decomposition of the electrolytic solution having been suppressed by the new organic solvent used for the organic electrolytic-solution rechargeable battery of this invention.

[0011]

[Example] Below, this invention is explained using a suitable example.

[0012] First, the lithium cobalt multiple oxide (LiCoO_2) of a positive active material was compounded as follows. Basic cobalt carbonate is pyrolyzed in air at the temperature of 650 degrees C for 24 hours, and it is tricobalt tetroxide (Co_3O_4). It compounded. a lithium carbonate and this tricobalt tetroxide -- lithium: -- it mixed so that a cobalt atomic ratio might be set to 1:1, and it pyrolyzed in air at the temperature of 700 degrees C for 16 hours

[0013] And the positive-electrode board was made as an experiment as follows. the lithium cobalt multiple-oxide 82 weight section obtained by the aforementioned method -- receiving -- N-methyl-2- as the polyvinylidene-fluoride 6.5 weight section, the graphite (Lonza SFG6) 10 weight section, the KETCHIEN black 1.5 weight section, and a solvent a pyrrolidone -- optimum dose addition -- you may carry out -- kneading -- a positive electrode -- a mixture -- the paste was prepared This paste was uniformly applied to the aluminum-gold network (0.1mm of wire sizes) of 100 meshes, at the temperature of 85 degrees C, 10-hour hot air drying and after burning at the temperature of 250 degrees C subsequently for 30 minutes, it pierced to the disk with a diameter of 16mm, and the lithium cobalt multiple-oxide electrode was made as an experiment. supposing, as for the geometric capacity of this electrode, occlusion and discharge of a 0.5 mols [per one mol (LiCoO_2) of active materials] lithium are done -- about 18 mAh(s) it is .

[0014] The negative-electrode board was made as an experiment as follows. the end of carbon powder (pyrolytic carbon) 92 weight section -- receiving -- N-methyl-2- as the polyvinylidene-fluoride 8 weight section and a solvent a pyrrolidone -- optimum dose addition -- you may carry out -- kneading -- a negative electrode -- a mixture -- the paste was prepared This paste was uniformly applied to SUS304 wire gauze (0.1mm of wire sizes) of 100 meshes, at the temperature of 85 degrees C, 10-hour hot air drying and after burning at the temperature of 250 degrees C subsequently for 30 minutes, it pierced to the disk with a diameter of 16mm, and the negative-electrode board was made as an experiment. the charge-and-discharge capacity of this electrode -- about 18 mAh(s) it is .

[0015] To the electrolytic solution, moreover, to the mixed solvent (2 volume ratio 1:3, 1: 1:1) of a sulfolane (below, it is written as S), and ethylene carbonate (below, it is written as EC) Three sorts of organic electrolytic solutions (below, it is written as LiClO_4 / (1M) S+EC (1:3), S+EC (1:2), and S+EC (1:1)) in which the one mol [/l.] lithium perchlorate (LiClO_4) was dissolved were used. These electrolytic solutions poured only the about 160micro liter of sum totals in positive, an aforementioned negative-electrode board, and an aforementioned separator, and were used for them. The organic electrolytic-solution rechargeable battery of this invention is called (A), (B), and (C), respectively. Moreover, i is the conventional electrolytic solution for comparison. LiClO_4 / (1M) PC+DME (1:1), LiClO_4 / (1M) PC+DEC (1:1) LiClO_4 /(1M)PC+EC (1:1), The conventional cell considered as the same composition as the organic electrolytic-solution cell (A) of this invention was produced except having used LiClO_4 / (1M) S+PC (1:1), LiClO_4 /(1M)EC, and LiClO_4 /(1M)S. a comparison cell -- respectively -- (**), (**), (**), (**), and (**) -- it is called [and / (mosquito)]

[0016] Drawing 1 is drawing of longitudinal section of a cell. It is the case which serves as the positive-electrode terminal which 1 pierced the stainless steel-aluminum-clad plate with a press and was processed in this drawing, and the obturation board which serves as the negative-electrode terminal into which 2 pierced a material of the same kind, and it was processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are carrying out sealing obturation by binding tight the inner circumference of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which is a positive electrode and serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

[0017] Next, terminal voltage is 4.1V at a 2.0mA constant current about these cells. It charges until it results, and it continues, and, similarly terminal voltage is 2.7V at a 2.0mA constant current. It applied to the discharging charge-and-discharge cycle-life examination (temperature of 85 degrees C) until it reached.

[0018] The result of a cycle examination is shown in drawing 2. As for the cell (A) of this invention, (B), and (C), the remarkable fall of service capacity is not seen until the number of charge-and-discharge cycles results in 100 times. However, the cell (a), the (b), the (c), the conventional (d), and the conventional (e) for comparison have the remarkable fall of the service capacity accompanying advance of a charge-and-discharge cycle. Moreover, service capacity is small although the fall of service capacity has few comparison cells (mosquito).

[0019] Thus, as compared with the conventional organic electrolytic-solution rechargeable battery, the maintenance property of the organic electrolytic-solution rechargeable battery of this invention which used the mixed solvent of S and EC for the electrolytic-solution solvent of the service capacity at the time of repeating a charge-and-discharge cycle improved remarkably.

[0020] In addition, although the above-mentioned example explained the case where a lithium cobalt multiple oxide was used as a positive active material, various things, such as manganese dioxide including 2 titanium sulfides, a spinel type lithium manganic acid ghost ($\text{Li}_x\text{Mn}_2\text{O}_4$), a vanadium pentoxide, and a molybdenum trioxide, can be used.

[0021] Although the above-mentioned example explained the case where the content of S in a solvent considered as 25, 33, and 50vol(s)% in 2 component solvent system, the same result will be obtained if the range of the content of S is about 10 vol(s)% - about 80 vol(s)%. The kind or concentration of a supporting electrolyte which are dissolved in such an organic solvent are not limited fundamentally, either. for example, LiAsF_6 , LiBF_4 , LiPF_6 , and LiCF_3SO_3 etc. -- one or more sorts can be used in the concentration of 0.5-2 mols/the about 1 range

[0022] Furthermore, in the above-mentioned example, although the example which uses a S+EC mixed solvent was shown, a stable solvent can be mixed and used electrochemically. Toluene, benzene, etc. are raised as an example.

[0023] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shape, or a paper form cell.

[0024]

[Effect of the Invention] Like the above, the organic electrolytic-solution rechargeable battery of this invention has few falls of the service capacity accompanying advance of a charge-and-discharge cycle.

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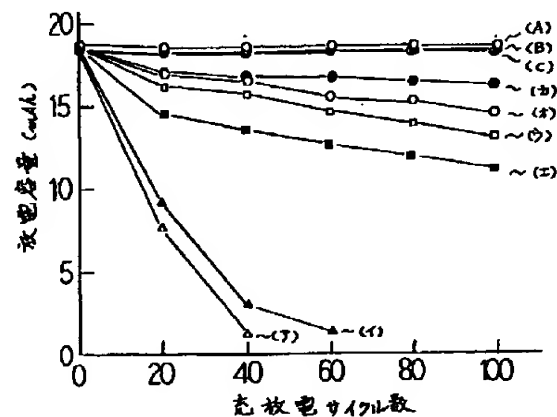
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(54)【発明の名称】 有機電解液二次電池

(57)【要約】

【目的】充放電サイクルの進行にともなう放電容量の低下が少ない有機電解液二次電池を得る。

【構成】リチウムイオンを吸蔵放出する物質からなる正極と、リチウムイオンを吸蔵放出する炭素材料を負極として備えた有機電解液二次電池において、スルホラン(S)とエチレンカーボネイト(EC)との混合溶媒を電解液溶媒として用いた。



【特許請求の範囲】

【請求項1】 リチウムイオンを吸蔵放出する物質からなる正極と、リチウムイオンを吸蔵放出する炭素材料を負極として備えた有機電解液二次電池において、スルホラン(S)とエチレンカーボネイト(EC)との混合溶媒を電解液溶媒として用いたことを特徴とする有機電解液二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、電子機器の駆動電源、メモリ保持電源あるいは電気自動車用電源としての高エネルギー密度でかつ高い安全性を有する有機電解液二次電池に関するものである。

【0002】

【従来の技術とその課題】電子機器の急激なる小形軽量化にともない、その電源である電池に対して小形で軽量かつ高エネルギー密度で、更に繰り返し充放電が可能な二次電池の開発への要求が高まっている。さらに、近年の環境問題への関心の高まりとともに電気自動車が注目を集めつつあり、その電源である電池に対しても小形で軽量かつ高エネルギー密度で、更に高温下(温度85℃)での繰り返し充放電が可能な二次電池の開発への要求が高まっている。これら要求を満たす二次電池として、有機電解液二次電池が最も有望である。

【0003】有機電解液二次電池の正極活物質には、二硫化チタンをはじめとしてリチウムコバルト複合酸化物、スピネル型リチウムマンガン酸化物、五酸化バナジウムおよび三酸化モリブデンなどの種々のものが検討されている。なかでも、リチウムコバルト複合酸化物(Li_xCoO_2)およびスピネル型リチウムマンガン酸化物($\text{Li}_x\text{Mn}_2\text{O}_4$)は、4V(Li/Li^+)以上のきわめて貴な電位で充放電を行うため、正極として用いることで高い放電電圧を有する電池が実現できる。

【0004】有機電解液二次電池の負極活物質は、金属リチウムをはじめとしてリチウムの吸蔵・放出が可能なLi-Al合金や炭素材料など種々のものが検討されているが、なかでも炭素材料は、安全性が高くかつサイクル寿命の長い電池が得られるという利点がある。

【0005】しかし、正極にリチウムコバルト複合酸化物(LiCoO_2)、スピネル型リチウムマンガン酸化物($\text{Li}_x\text{Mn}_2\text{O}_4$)などを用い、負極に炭素材料を用いた電池は、高温(温度85℃)下での充放電サイクルの進行にともなって放電容量が急激に低下するという問題があった。例えば、プロピレンカーボネイト(PC)と1,2-ジメトキシエタン(DME)との混合溶媒に過塩素酸リチウム(LiClO_4)を溶解した電解液を用いたコイン電池は、充放電を繰り返すと放電容量が急激に減少した。これは、正極によって、電解液が酸化分解されたことに起因するものと考えられる。

【0006】最近、このような高電圧の電池系において

実用可能な耐酸化性能に優れた有機電解液として、プロピレンカーボネイト(PC)とジエチルカーボネイト(DEC)との混合溶媒を用いると、前記の放電容量の低下が抑制されることが報告された(第32回電池討論会要旨集 p.31(1991))。

【0007】しかし、我々が上記電解液について検討した結果、上記有機溶媒の電気化学的安定性が依然不十分であることがわかった。

【0008】そこで、電解液の電気化学的安定性をさらに向上した電解液の開発が求められていた。

【0009】

【課題を解決するための手段】本発明は、リチウムイオンを吸蔵放出する物質からなる正極と、リチウムイオンを吸蔵放出する炭素材料を負極として備えた有機電解液二次電池において、スルホラン(S)とエチレンカーボネイト(EC)との混合溶媒を用いることによって、上記問題を解決しようとするものである。

【0010】

【作用】本発明の有機電解液二次電池は、従来の有機電解液二次電池に比較して高温下で充放電サイクルを繰り返した場合の放電容量の保持特性が優れているという作用がある。これは、本発明の有機電解液二次電池に用いた新しい有機溶媒によって、電解液の分解が抑制されたことに起因するものと考えられる。

【0011】

【実施例】以下に、好適な実施例を用いて本発明を説明する。

【0012】まず、正極活物質のリチウムコバルト複合酸化物(LiCoO_2)をつぎのように合成した。塩基性炭酸コバルトを温度650℃で24時間、空気中で熱分解して四三酸化コバルト(Co_3O_4)を合成した。炭酸リチウムとこの四三酸化コバルトとをリチウム：コバルト原子比が1：1になるように混合して温度700℃で16時間、空気中で熱分解した。

【0013】そして、正極板を次のように試作した。前記の方法で得られたリチウムコバルト複合酸化物82重量部に対してポリフッ化ビニリデン6.5重量部、グラファイト(ロンザ製SFG6)10重量部、ケッチェンブラック1.5重量部および溶剤としてのN-メチル-2-ピロリドンを適量添加してよく混練し正極合剤ペーストを調製した。このペーストを100メッシュのアルミ金網(線径0.1mm)に均一に塗布し、温度85℃で10時間熱風乾燥、次いで温度250℃で30分焼き付けした後、直径16mmの円板に打ち抜いてリチウムコバルト複合酸化物電極を試作した。この電極の理論容量は、活物質(LiCoO_2)1モル当り、0.5モルのリチウムが吸蔵・放出されるとすると、約18mAhである。

【0014】負極板は、次のように試作した。炭素粉末(熱分解炭素)92重量部に対してポリフッ化ビニリデン8重量部および溶剤としてのN-メチル-2-ピロリドン

を適量添加してよく混練し、負極合剤ペーストを調製した。このペーストを100メッシュのSUS304金網（線径0.1mm）に均一に塗布し、温度85℃で10時間熱風乾燥、次いで温度250℃で30分焼き付けした後、直径16mmの円板に打ち抜いて負極板を試作した。この電極の充放電容量は、約18mAhである。

【0015】また、電解液にはスルホラン（以下ではSと表記する）とエチレンカーボネイト（以下ではECと表記する）との混合溶媒（体積比で1:3, 1:2, 1:1）に、1モル/lの過塩素酸リチウム（ LiClO_4 ）を溶解させた3種の有機電解液（以下では LiClO_4 (1M)/S+EC(1:3), S+EC(1:2), S+EC(1:1)と表記する）を用いた。これらの電解液は、前記の正、負極板およびセパレーターに合計約160マイクロリッターだけ注液して用いた。本発明の有機電解液二次電池をそれぞれ（A）、（B）および（C）と呼ぶ。また、比較のために従来の電解液である LiClO_4 (1M)/PC+DME(1:1), LiClO_4 (1M)/PC+DEC(1:1), LiClO_4 (1M)/PC+EC(1:1), LiClO_4 (1M)/S+PC(1:1), LiClO_4 (1M)/EC, LiClO_4 (1M)/Sを用いた以外は、本発明の有機電解液電池（A）と同様の構成とした従来の電池を作製した。比較電池をそれぞれ（ア）、（イ）、（ウ）、（エ）、（オ）および（カ）と呼ぶ。

【0016】図1は、電池の縦断面図である。この図において1は、ステンレス-アルミークラッド鋼板をプレスによって打ち抜き加工した正極端子を兼ねるケース、2は同種の材料を打ち抜き加工した負極端子を兼ねる封口板であり、その内壁には負極3が当接されている。5は有機電解液を含浸したポリプロピレンからなるセパレーター、6は正極であり正極端子を兼ねるケース1の開

口端部を内方へかしめ、ガスケット4を介して負極端子を兼ねる封口板2の内周を締め付けることにより密閉封口している。

【0017】次に、これらの電池を2.0mAの定電流で、端子電圧が4.1Vに至るまで充電して、つづいて、同じく2.0mAの定電流で、端子電圧が2.7Vに達するまで放電する充放電サイクル寿命試験（温度85℃）にかけた。

【0018】サイクル試験の結果を、図2に示す。本発明の電池（A）、（B）および（C）は、充放電サイクル数が100回に至るまで放電容量の著しい低下がみられない。しかし、比較のための従来の電池（ア）、（イ）、（ウ）、（エ）および（オ）は、充放電サイクルの進行に伴う放電容量の低下が著しい。また、比較電

池（カ）は放電容量の低下は少ないものの放電容量が小さい。

【0019】このように、電解液溶媒にSとECとの混合溶媒を用いた本発明の有機電解液二次電池は従来の有機電解液二次電池と比較して、充放電サイクルを繰り返した場合の放電容量の保持特性が著しく向上した。

【0020】なお、上記実施例では正極活物質としてリチウムコバルト複合酸化物を用いる場合を説明したが、二硫化チタンをはじめとして二酸化マンガン、スピネル型リチウムマンガン酸化物（ $\text{Li}_x\text{Mn}_2\text{O}_4$ ）、五酸化バナジウムおよび三酸化モリブデンなどの種々のものを用いることができる。

【0021】上記実施例では、2成分溶媒系において溶媒中のSの含有量が25.33および50vol%とした場合を説明したが、Sの含有量が約10vol%〜約80vol%の範囲であれば、同様な結果が得られる。このような有機溶媒に溶解される支持電解質の種類や濃度も基本的に限定されるものではない。たとえば、 LiAsF_6 , LiBF_4 , LiPF_6 , LiCF_3SO_3 などの1種以上を、濃度0.5〜2モル/l程度の範囲で用いることができる。

【0022】さらに、上記実施例ではS+EC混合溶媒を用いる例を示したが電気化学的に安定な溶媒を混合して使用することができる。例としては、トルエン、ベンゼンなどがあげられる。

【0023】なお、前記の実施例に係る電池はいずれもコイン形電池であるが、円筒形、角形またはペーパー形電池に本発明を適用しても同様の効果が得られる。

【0024】

【発明の効果】以上のごとく、本発明の有機電解液二次電池は、充放電サイクルの進行にともなう放電容量の低下が少ない。

【図面の簡単な説明】

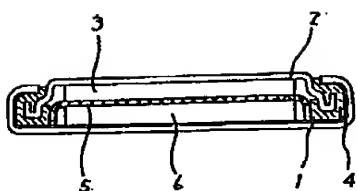
【図1】非水電解質二次電池の一例であるボタン電池の内部構造を示した図。

【図2】試験電池のサイクルと放電容量を示した図。

【符号の説明】

- 1 電池ケース
- 2 封口板
- 3 負極
- 4 ガスケット
- 5 セパレーター
- 6 正極

【図1】



【図2】

